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# Coherent Electronic Coupling versus Localization in Individual Molecular Dimers

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We have investigated electronic excitation transfer in individual molecular dimers by time and spectrally resolved confocal fluorescence microscopy. The single molecule measurements allow for directly probing the distribution of the electronic coupling strengths due to static disorder in the polymer host. We find dimers where the excitation is delocalized (superradiant emission) while for others emission originates from a localized state. Transitions between delocalized and localized states as observed for a given dimer are attributed to structural fluctuations of the guest-host system.

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Coherent energy transport is a controversial issue in molecular aggregates like light-harvesting pigments [1–3], J aggregates [4], and conjugated polymers [5,6]. While the coherent excitation transfer interaction tends to delocalize the excitation energy among molecules, static and dynamical disorder tend to localize it. It has been shown experimentally [7,8] as well as theoretically [9,10] that cooperative spontaneous emission (superradiance) is an appropriate measure of intermolecular coherence or the exciton delocalization length. In particular, it has been pointed out in [10] that single molecule spectroscopy would be the appropriate tool to determine the distribution of cooperative radiative decay rates in molecular aggregates. For a simple molecular dimer consisting of two coupled oscillators the radiative rate  $k_{\text{rad}}$  of the dimer should be twice the value of the monomer, if the excitation is completely delocalized yielding a superradiance coherence factor  $L_S$  of 2. [ $L_S = k_{\text{rad}}(\text{dimer})/k_{\text{rad}}(\text{monomer})$ .] In this Letter we show by single molecule spectroscopy of individual molecular dimers [11–14] with a fairly large electronic coupling strength that the superradiance coherence sizes are widely distributed directly reflecting the interplay between intermolecular coupling and static disorder introduced by the polymer host. The chemical structure of the dimer allows for distinguishing localized and delocalized states by their particular emission spectra, too. At room as well as liquid helium temperatures we experimentally can track delocalization of an initially localized state and vice versa. The temporal fluctuations of the electronic coupling strength are attributed to structural fluctuations of the guest-host system. As the molecular environments in solids are in general not stable, these findings impose fundamental limits to the control of coherent energy transport and molecular entanglement in solids [12].

The simplest type of a molecular aggregate is composed of two identical chromophores. We investigate bi-peryleneimide (BPM) dimers in which two peryleneimide molecules (PM) are covalently held together at a

fixed distance by a single bond. In Fig. 1(a) the conformation of the electronic ground state of BPM as obtained by quantum-chemical electronic structure optimizations is shown. The dihedral angle between the two PM moieties amounts to  $82^\circ$  which indicates that  $\pi$ - $\pi$  overlap is negligible. Accordingly, we have assumed a purely electrostatic interaction [15,16] to calculate the excitation transfer interaction  $J$ . For the given geometry of the dimer  $J$  is negative ( $J = -435 \text{ cm}^{-1}$ ), and only the transition to the lower exciton state  $\Omega_-$  carries oscillator strength (the upper state  $\Omega_+$  is dark). The salient features of our approach can be qualitatively recovered in the absorption and emission spectra of BPM, which show

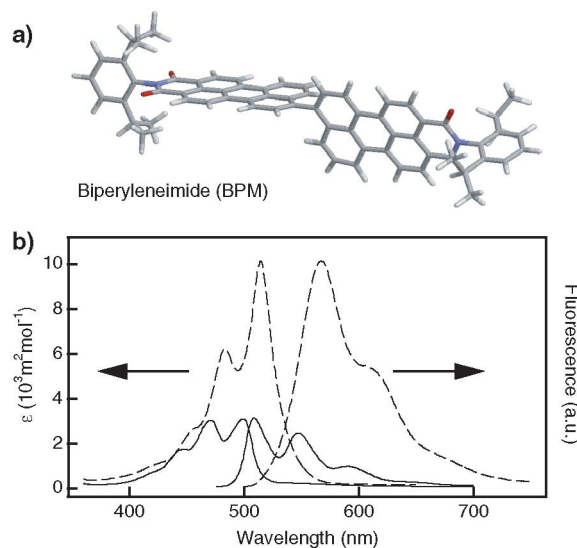


FIG. 1 (color online). (a) Molecular structure of the electronic ground state of bi-peryleneimide (BPM). The transition dipoles of the peryleneimide (PM) monomers are aligned along the long molecular axes. (b) Absorption and fluorescence spectra of tetradecane solutions of PM (solid line) and BPM (dashed line).

the expected redshift and redistribution of oscillator strength with respect to PM [Fig. 1(b)].

When embedding BPM in an amorphous polymer (Zeonex®), the transition energies of the two PM monomers in general are not degenerate (diagonal disorder). The exciton levels  $\Omega_{\pm}$  in the dimer then become

$$\Omega_{\pm} = (\omega_1 + \omega_2)/2 \pm \{[(\omega_1 - \omega_2)/2]^2 + J^2\}^{1/2}, \quad (1)$$

with  $\omega_1, \omega_2$  being the transition frequencies of the monomers. To get an idea of the spread of emission frequencies or the static disorder  $\sigma$ , we have measured the emission spectra of a number of single PM monomers embedded in a Zeonex film. From this distribution we calculate that  $\sigma \approx 260 \text{ cm}^{-1}$ . For an ensemble of dimers the ratio  $\sigma/J$  is a measure of the average extent of delocalization. In case of large static disorder ( $\sigma \gg |J|$ ) the excitation is localized, while for  $\sigma \ll |J|$  the excitation is delocalized. Therefore, on average the excitation energy should have a tendency to be delocalized for BPM in Zeonex. It is, however, important to note that in our experiments we are addressing single dimers where the site energy difference  $|\omega_1 - \omega_2|$  may be much larger (or smaller) than the average static disorder  $\sigma$ . Considerable variations of  $J$  (off-diagonal disorder) which also would change the ratio  $\sigma/J$  are highly unlikely because the interchromophore distance is fixed and the only other relevant degree of freedom in the dimer—the dihedral angle between the two moieties—will only slightly influence  $J$  if showing a large distribution at all.

In Fig. 2 we present fluorescence spectra of two individual BPM dimers together with an ensemble fluorescence spectrum, which have been recorded in a homebuilt scanning confocal optical microscope [11]. A cw-Ar<sup>+</sup>-ion laser operated at 488 nm was used for excitation, and the spectra were taken with an imaging spectrograph equipped with a liquid-nitrogen cooled charge coupled

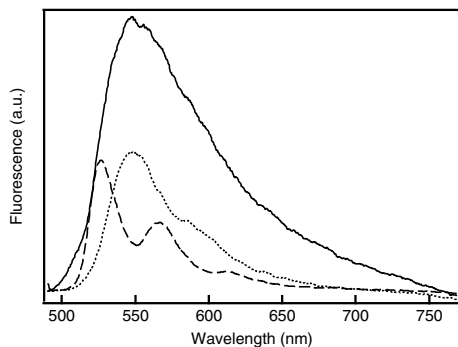


FIG. 2. Room temperature fluorescence spectra of BPM in a thin polymer film (Zeonex). Fluorescence spectrum of an ensemble of BPM molecules (solid line). Type I emission spectrum of a single BPM molecule (dotted line). Type II emission spectrum of another single BPM molecule (dashed line). Type I spectra represent the strong coupling case (delocalization), type II spectra the weak coupling case (localization).

device camera. The two distinct spectra in Fig. 2 recorded for individual molecules denoted types I and II obviously cannot be distinguished in the ensemble spectrum. Comparison to bulk solution emission spectra of the BPM dimer and the PM monomer [Fig. 1(b)] suggests that type I spectra represent emission from the delocalized lower exciton state while type II spectra are attributed to monomer-type emission from a localized state. The loss of vibronic structure in type I spectra is attributed to a collective mode operative in the exciton state [17]. In particular, we assume that a low frequency torsional motion in the soft interchromophore potential couples strongly to the delocalized electronic excitation smearing out the vibronic structure. This view is corroborated by the solution emission spectra of BPM [Fig. 1(b)] where the appreciable Stokes shift points to a motion towards a more planar structure in the excited state.

We have measured simultaneously fluorescence intensities, lifetimes, and emission spectra of BPM as a function of time. In Fig. 3 complete data sets are shown for two individual BPM dimers. For these experiments, the

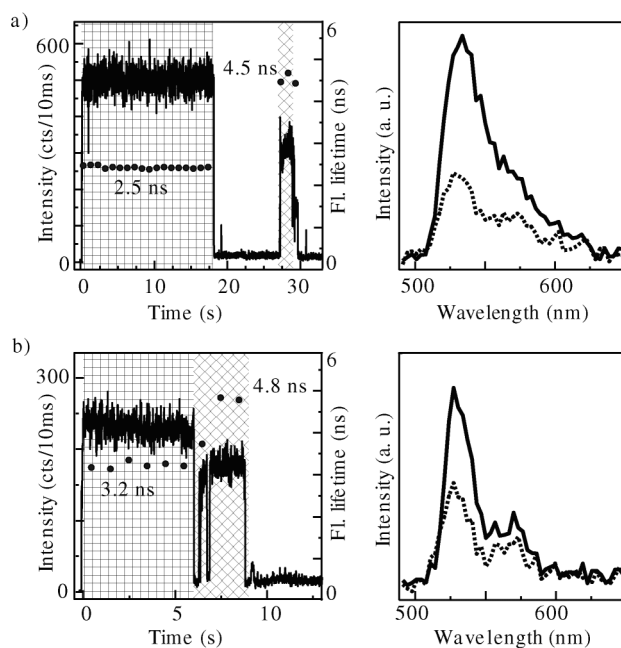


FIG. 3. Room temperature measurements of the fluorescence lifetimes and spectra of two single BPM dimers (a) and (b) before and after one of the PM chromophores has bleached. Left panel: The signal drop after the dark state ( $\sim 16$ – $27$  s) in the fluorescence intensity trajectory indicates the bleaching of one of the PM chromophores [11]. After the bleaching event the fluorescence lifetime ( $\bullet$ ) has increased from 2.5 to 4.5 ns for molecule (a) and from 3.2 to 4.8 ns for molecule (b) yielding superradiance coherence size factors of  $L_S = 1.8$  and  $L_S = 1.5$ , respectively. Right panel: Fluorescence spectra recorded during the time intervals marked in the intensity trace by cross-hatch (spectrum represented by solid line) and diagonal hatch (spectrum represented by dotted line).

excitation light source was a frequency-doubled Ti:sapphire laser ( $\lambda = 457$  nm) delivering light pulses with a width of about 1 ps, and a single-photon avalanche photodiode attached to a time-correlated single-photon counting board was used for time-resolved detection of fluorescence. Single exponentials were fitted to the fluorescence decay curves by maximum likelihood estimation [18] to determine the fluorescence lifetimes. For both molecules shown in Fig. 3 the fluorescence intensity has dropped to a lower level after a reversible dark state indicating that one of the chromophores has bleached [11]. Also, in both cases the fluorescence lifetime  $\tau_f$  has increased after the bleaching event, when emission occurs from a single chromophore. An important difference, however, is given by the ratio of the fluorescence lifetimes, which shows that  $L_S$  is different for the two dimers. The value of  $L_S = 1.8$  for the data in Fig. 3(a) is close to  $L_S = 2$  as would be expected for full excitation delocalization. The discrepancy may be partly attributed to the fact that we implicitly assumed the relation  $\tau_f^{-1} \sim k_{\text{rad}}$  to hold. The fluorescence yield  $\Phi_f$  of the PM monomer, however, was reported [19] to be smaller than 1 ( $\Phi_f \sim 0.95$ ) and may be slightly different for the dimer and the monomer. Quenching of the monomer by the final bleaching product [11] seems to be highly unlikely because for PM in solution we find  $\tau_f \sim 4.4$  ns which is similar to the value found after the first chromophore bleached (Fig. 3). Along these lines we conclude that the fluorescence lifetime changes in Fig. 3(a) give clear evidence for cooperative spontaneous emission in this BPM dimer. The lifetime changes are accompanied by changes of the shape of the emission spectra. As shown in Fig. 3(a), we observe a transition from a spectrum with basically no vibronic structure to a spectrum with a more pronounced vibronic structure, i.e., two emission bands. The first spectrum resembles the type I spectrum of Fig. 2 while the second one appears to be type II. Supported by the lifetime data, we interpret type I spectra to represent emission from the delocalized exciton state. Type II spectra obviously can arise due to different reasons. For the data shown in Fig. 3(a), bleaching of the first chromophore in the dimer inevitably leads to emission from the monomer. In Fig. 2, however, the type II spectrum is due to emission from a localized state within an intact dimer where coherent coupling has been lifted by static disorder. The two proximate PM chromophores will now communicate by incoherent Förster-type energy hopping [19] (weak coupling) eventually giving rise to emission from a single chromophoric site.

In Fig. 3(b) data for another dimer are presented. The smaller value of  $L_S = 1.5$  is mainly attributed to the longer fluorescence lifetime ( $\tau_f \sim 3.2$  ns) of the original dimer state. Following our discussion, we assume that in this dimer we observe the regime of intermediate coupling where the excitation is not fully delocalized. This view is supported by the emission spectra. While the

spectrum following the bleaching event is clearly type II, the original spectrum appears to be a mixture of types I and II because it already shows the second emission band but with weaker intensity than seen in Fig. 2. In this context it is important to realize that the single dimer spectra shown in Fig. 2 represent the “pure” cases, i.e., emission from delocalized (type I) and localized (type II) states.

By investigation of 30 isolated BPM dimers we find  $L_S$  values ranging from 1 to 1.8 [10] and a distribution of emission spectra with spectral shapes within the limits given by types I and II in Fig. 2. These results quite nicely reflect the interplay between the coherent excitation transfer interaction and static disorder. It is an intriguing observation that in BPM not only the fluorescence lifetimes but also the shape of the emission spectra reflect the degree of excitation delocalization.

Besides variations in intermolecular coupling between different dimers we interestingly also have observed temporal variations for a single dimer. In Figs. 4(a) and 4(b) we have plotted the fluorescence intensity and spectra of a single dimer as a function of time. At the beginning of the experiment spectrum 1 indicates emission from a localized state (type II). After some time the emission changes instantaneously to type I (spectrum 2) now representing the coherent coupling case. With time advancing there are additional transitions from localization to delocalization and vice versa until irreversible photobleaching occurs. With the same arguments as presented before, we can largely exclude time-dependent variations of the coupling strength  $J$  to be responsible for the observed changes. Fluctuations of the nuclear coordinates of the guest-host system occurring on a broad range of time scales can lead to appreciable shifts of the electronic spectra. In accordance with other investigations [20,21] we have observed spectral shifts of the emission spectra of single PM monomers in Zeonex as large as 10–20 nm at room temperature. It is therefore reasonable to assume that shifts of the transition frequencies  $\omega_1, \omega_2$  induce transitions from the localized to the delocalized state and vice versa. For single sulforhodamine molecules in poly(methyl methacrylate) it was found that spectral fluctuations could be spontaneous as well as light induced [21]. In any case such spectral fluctuations are attributed to changes of configurational coordinates of the system. At present we cannot decide whether the internal degrees of freedom of BPM are involved here or structural fluctuations of the amorphous polymer host. Nevertheless we point out that while a change of the ground state dihedral angle of BPM will not influence the coupling strength  $J$  it might very well influence the transition frequencies  $\omega_1$  and  $\omega_2$  to various extents.

The dynamic changes between localized and delocalized states and their spectral consequences can be observed down to liquid helium temperatures [22]. In Fig. 4(c) a transition from the localized (I) to the

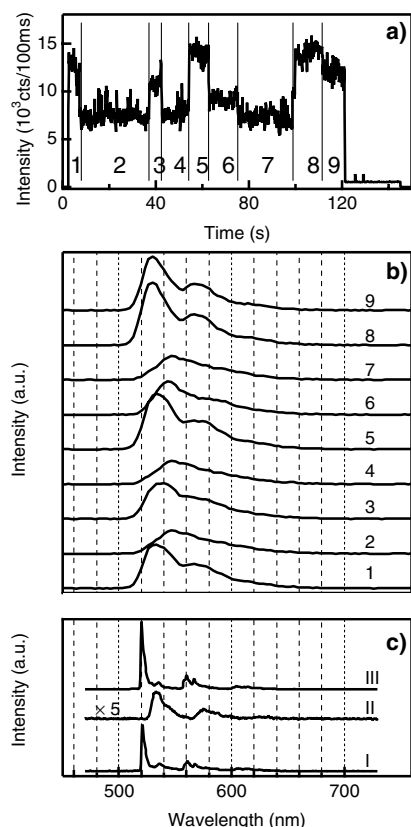


FIG. 4. Temporal variations of the electronic coupling strength of individual BPM dimers. (a) Fluorescence intensity trajectory of a single BPM dimer recorded during the time intervals numbered correspondingly in (a). The fluctuations in spectral shape and position reflect transitions between localized (1, 3, 5, 8, 9) and delocalized states (2, 4, 6, 7) of the dimer. These measurements have been conducted at room temperature. (c) Fluorescence spectra of a single BPM dimer recorded at 1.4 K. Again spectral fluctuations are observed as a function of time (I:  $t = 0$  s; II:  $t = 40$  s; III:  $t = 80$  s).

delocalized (II) and back to the localized (III) state is shown for a single BPM dimer. The emission from the localized state is characterized by sharp zero-phonon lines (I, III). These are absent (II) in case of excitation delocalization supposedly because of the interchromophore torsional mode, which has been discussed before and gives rise to strong electron-phonon coupling. As for the room temperature measurements we assume spectral shifts induced by spatial fluctuations of the guest-host system to trigger the fluctuations in electronic coupling strength. Similar fluctuations at 1.4 K have been deduced recently from polarization dependent measurements within the 8-membered B800 ring of light-harvesting complexes [23]. We therefore expect this phenomenon to be quite general and not restricted to specific molecular structures or experimental conditions. Finally, we want to

emphasize that single molecule spectroscopy is the necessary tool to probe such fluctuations, which would be drowned in the ensemble average.

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- [1] V. Sundström, T. Pullerits, and R. van Grondelle, *J. Phys. Chem. B* **103**, 2327 (1999).
- [2] A. M. van Oijen, M. Ketelaars, J. Köhler, T. J. Aartsma, and J. Schmidt, *Science* **285**, 400 (1999).
- [3] M. A. Bopp, A. Sytnik, T. D. Howard, R. J. Cogdell, and R. M. Hochstrasser, *Proc. Natl. Acad. Sci. U.S.A.* **96**, 11 271 (1999).
- [4] H. Fidder, J. Knoester, and D. Wiersma, *J. Chem. Phys.* **95**, 7880 (1991).
- [5] R. H. Friend *et al.*, *Nature (London)* **397**, 121 (1999).
- [6] J. Yu, D. H. Hu, and P. F. Barbara, *Science* **289**, 1327 (2000).
- [7] R. Monshouwer, M. Abrahamsson, F. van Mourik, and R. van Grondelle, *J. Phys. Chem. B* **101**, 7241 (1997).
- [8] S. De Boer and D. A. Wiersma, *Chem. Phys. Lett.* **165**, 45 (1990).
- [9] T. Meier, Y. Zhao, V. Chernyak, and S. Mukamel, *J. Chem. Phys.* **107**, 3876 (1997).
- [10] Y. Zhao, T. Meier, W. M. Zhang, V. Chernyak, and S. Mukamel, *J. Phys. Chem. B* **103**, 3954 (1999).
- [11] T. Christ, F. Petzke, P. Bordat, A. Herrmann, E. Reuther, K. Müllen, and Th. Basché, *J. Lumin.* **98**, 23 (2002).
- [12] C. Hettich, C. Schmitt, J. Zitzmann, S. Kühn, I. Gerhardt, and V. Sandoghdar, *Science* **298**, 385 (2002).
- [13] J. Hernando, M. van der Schaaf, E. van Dijk, M. Sauer, M. F. Garcia-Parajo, and N. F. van Hulst, *J. Phys. Chem. A* **107**, 43 (2003).
- [14] T. Vösch, M. Cotlet, J. Hofkens, K. van der Biest, M. Lor, K. Weston, P. Tinnefeld, M. Sauer, L. Latterini, K. Müllen, and F. C. De Schryver, *J. Phys. Chem. A* **107**, 6920 (2003).
- [15] M. Kasha, H. Rawls, and M. Ashraf El-Bayoumi, *Pure Appl. Chem.* **11**, 371 (1965).
- [16] S. Tretiak, W. M. Zhang, V. Chernyak, and S. Mukamel, *Proc. Natl. Acad. Sci. U.S.A.* **96**, 13003 (1999).
- [17] T. Pauck, H. Bässler, J. Grimme, U. Scherf, and K. Müllen, *Chem. Phys.* **210**, 219 (1996).
- [18] L. Brand, C. Eggeling, C. Zander, K. H. Drexhage, and C. A. M. Seidel, *J. Phys. Chem. A* **101**, 4313 (1997).
- [19] M. Maus *et al.*, *J. Am. Chem. Soc.* **123**, 7668 (2001).
- [20] J. J. Macklin, J. K. Trautman, T. D. Harris, and L. E. Brus, *Science* **272**, 255 (1996).
- [21] H. P. Lu and X. S. Xie, *Nature (London)* **385**, 143 (1997).
- [22] T. Christ, F. Kulzer, T. Weil, K. Müllen, and Th. Basché, *Chem. Phys. Lett.* **372**, 878 (2003).
- [23] C. Hofmann, M. Ketelaars, M. Matsushita, H. Michel, T. J. Aartsma, and J. Köhler, *Phys. Rev. Lett.* **90**, 013004 (2003).